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⑤④ **Flaky aluminium pigments coated with molybdic acid.**

⑤⑦ **Aluminium flakes coated with molybdic acid in an amount of 0.1 to 10% by weight in terms of Mo based on Al.**

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The present invention relates to aluminium pigments which are incorporated into water base paints used for finish coating car bodies and the like and water base inks.

The aluminium pigments to be incorporated in the water base paints are described in many prior publications. However, processes for obtaining the aluminium pigments which can be incorporated in the water base paints used for finish coating the car bodies are described in only JP-B-01/54386, JP-A-59/74201 and JP-B-60/8057.

JP-B-01/54386 relates to a treatment with chromic acid. By this treatment, the aluminium pigment which has a good stability in the water base paint, which can inhibit the production of hydrogen gas and which is excellent in color tone can be obtained. When the aluminium pigment comprises fine aluminium flakes, however, this treatment causes the dissolution of the fine aluminium flakes. Thus, the aluminium pigment comprising the fine aluminium flakes having an average particle size (D_{50}) of less than 20 μm is hardly obtained. Further, this treatment causes industrial hygienic and environmental problems due to the use of Cr(VI) and therefore, its application is limited.

JP-A-59/74201 relates to a treatment with ammonium vanadate. By this treatment, the gas production is inhibited. However, this treatment causes the increase in thickness of a coating and the lowering in color tone and therefore, its application is limited.

JP-B-60/8057 relates to a treatment with a laury ester of phosphoric acid. By this treatment, the aluminium pigment which inhibits the gas production and has the good color tone can be obtained. This treatment gives an important defect to properties of the coating due to the presence of lauryl group on the surface of the coating. The coating having the defective property shows poor adhesion with a metallic base coating film and a top coating film, when the water base paint containing the resultant aluminium pigment is used for finish coating the car body according to a standard coating method such as a 2C1B coating method and a 2C2B coating method.

As described in the above, there is no prior art which can provide the aluminium pigment suitable for the incorporation in the water base paint used for finish coating the car body, which is excellent in the color tone, the stability in the water base paint and the coating property.

An object of the present invention is to provide the aluminium pigment suitable for the incorporation in the water base paint used for finish coating the car body, which is excellent in the color tone, the stability in the water base paint and the coating property.

Accordingly, the present invention provides an aluminium pigment suitable for a water base paint comprising aluminium flakes, the surface of each aluminium flake being coated with a coating of molybdic acid in an amount of 0.1 to 10 % by weight in terms of Mo based on aluminium.

The aluminium pigment according to the present invention is prepared by reacting the aluminium flakes with an alkaline aqueous solution containing ammonium molybdate, whereby the coatings of molybdic acid in an amount of 0.1 to 10 % by weight in terms of Mo based on aluminium are formed on the aluminium flakes.

As the aluminium flakes, the aluminium flakes having the excellent color tone, that is, the aluminium flakes being rich in metallic luster which has average particle diameter (D_{50}) of about 1 to 50 μm , preferably about 10 to 30 μm can be used. These aluminium flakes are produced by grinding or milling using a grinding agent in the presence of a grinding medium in a suitable device such as a ball mill or an attritor mill. As the grinding agent, a higher fatty acid such as oleic acid, stearic acid, isostearic acid, lauric acid, palmitic acid and myristic acid; aliphatic amines; aliphatic amides; and aliphatic alcohols are generally used.

Desirably, the aluminium flakes to be treated is previously dispersed in a water-soluble solvent mentioned below so that they are easily wet with the alkaline aqueous solution containing ammonium molybdate as a treating solution. In case of that the grinding medium is incompatible with the treating solution, the grinding medium should be replaced with the water-soluble solvent prior to the treatment.

Usable ammonium molybdate is either of ortho-, meta- or para-molybdate. Alkali metal molybdate which is also water-soluble is not preferable for the treatment of the aluminium flakes, because of its high alkaline strength. Further, if the alkali metal remains in the coating, the remaining alkali metal may affect the coating properties. In the preparation of the treating solution, ammonium molybdate is preferably dissolved in a mixture of water and the water-soluble solvent so that it is contained at the concentration of a few % or less. The water-soluble solvent is essential for effecting the contact of the aluminium flakes and ammonium molybdate.

Usable water-soluble solvent includes ethylene glycol monobutyl ether (butyl cellosolve), diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monopropyl ether and isopropyl alcohol.

When the aluminium flakes are contacted with the treating solution, the treating solution should be alkaline. In general, the pH of the treating solution is 7 to 10, preferably 7.5 to 9.5, more preferably 8 to 9 and most preferably 8.3 to 8.9. When the pH is less than 7, the reaction of aluminium with molybdate proceeds very slowly, perhaps due to the presence of the grinding agent such as the fatty acid adsorbed on the surfaces of

the aluminium flakes. Of course, when the treating solution has the acidic pH which is out of the passive zone, the dissolution of aluminum is happened. On the other hand, when the pH of the treating solution is above 10, the rapid reaction is happened and as the result, the aluminium pigment excellent in the color tone cannot be obtained.

5 The reaction is completed by removing the water and unreacted reactants from a reaction system. After the reaction has been completed, a reaction product is washed and filtered. If necessary, the resultant residue is dispersed in the water-soluble solvent so as to store stably.

The amount of the resultant coating of molybdic acid is in the range of 0.1 to 10 % by weight in terms of Mo based on aluminium. When it is less than the lower limit, the inhibition of the gas production is insufficient. 10 On the other hand, when it is above the upper limit, the coating is too thick and as the result, the color tone is impaired. Preferable amount is 0.1 to 3 % by weight.

As shown in the following examples, the aluminium pigment having the desired properties can be obtained by treating the aluminium flakes with an alkaline aqueous solution containing ammonium molybdate (hereinafter referred to as "first treatment"). By subjecting the aluminium pigment prepared in the first treatment to a 15 second treatment mentioned below, the aluminium pigment having the desired properties can be obtained more certainly.

The second treatment comprises mixing and kneading the first-treated aluminium pigment with a second treating agent selected from water-insoluble metal salts of molybdic acid and vanadium pentoxide so that 0.1 to 10 % by weight of the treating agent in terms of metal based on aluminium is attached on the above coating 20 of molybdic acid. When the first-treated aluminium pigment contains water, the water is preferably replaced with the water-soluble solvent before the first-treated aluminium pigment is subjected to the second treatment.

Usable water-insoluble metal salts of molybdic acid as the second treating agent include basic zinc salt, magnesium salt, calcium salt, strontium salt and barium salt. The second treating agent is powder, generally having average particle size of about 1 to 10 μm . It is used after dispersing in a small amount of the water-soluble solvent. 25

The powdery second treating agent together with the first-treated aluminium pigment are dispersed in the water-soluble solvent followed by mixing and kneading, thereby the powder of the second treating agent is attached on the coatings of the molybdic acid formed in the first treatment. The amount of the powdery second treating agent attached on the coating of molybdic acid by the second treatment is in the range of 0.1 to 10 % 30 by weight in terms of metal based on aluminium. When it is less than the lower limit, the advantage of the second treatment cannot be obtained. On the other hand, when it is above the upper limit, the attached amount of the powdery second treating agent is too much and as the result, the color tone is impaired. Preferable amount is 1 to 8 % by weight.

Usually, the powdery second treating agent used is not completely attached on the coating of molybdic acid. Because the second treating agent itself is stable in the water base paint and does not affect the coating 35 properties, the powdery second treating agent in unattached condition may be present during the preparation of the water base paint.

For increasing the attached amount of the powdery second treating agent on the coatings of molybdic acid, it is preferable to contact the first-treated aluminium pigment with an aqueous solution of ammonium phosphate or an alcoholic solution of lower alkyl ester of orthophosphoric acid after forming the coatings of molybdic acid, 40 for example during the washing of the first-treated aluminium pigment. It is assumed that by such a contact, phosphate (-P-OH) groups are adsorbed on the coatings of molybdic acid, thereby the adhesion of the powdery second treating agent to the coatings of molybdic acid can be increased. Alternatively, the surface of the second treating agent may be modified with the phosphate (-P-OH) groups prior to the use.

45 The second-treated aluminium pigment has a structure that the coatings of molybdic acid in an amount of 0.1 to 10 % by weight in terms of Mo based on aluminium are formed on the aluminium flakes and further at least one of the powdery second treating agent selected from the water-insoluble metal salts of molybdic acid and vanadium pentoxide in the amount of 0.1 to 10 % by weight in terms of metal based on aluminium is attached on the coatings of molybdic acid.

50 The aluminium pigment of the present invention is incorporated in any of the water base paint. The type of the water base resin constituting the water base paint is classified into a water soluble resin, a water dispersible resin and an emulsifiable resin. The nature of the water base resin includes a combination of acrylic and melamine resins, a combination of polyester and melamine resins, urethane resin and CAB resin. The type and the nature of the water resin to which the aluminium pigment of the present invention is applied is not limited. 55 Of course, the water base paint in which the aluminium pigment of the present invention is incorporated is coated by any coating method. The known coating methods such as an air spray coating, an airless spray coating and a roller coating can be used.

According to the present invention, by treating the aluminium flakes with the alkaline aqueous solution

containing ammonium molybdate in the first treatment, the coatings of molybdic acid which is excellent in water resistance can be formed on the aluminium flakes without lowering the intrinsic color tone of the aluminium pigment due to the slow reaction with the alkaline aqueous solution containing ammonium molybdate. And, by subjecting the first-treated aluminium pigment to the second treatment using the powdery second treating agent selected from the water-insoluble metal salt of molybdic acid and vanadium pentoxide, the powders of the second treating agent are attached on the coatings of molybdic acid, thereby the water resistance of the aluminium pigment can be further improved. The water base paint in which the second-treated aluminium pigment is incorporated is very excellent in storage stability, as compared with the prior water base paints. As clear from the following examples, the treatment according to the present invention does not cause the lowering of the coating properties and therefore, the aluminium pigment of the present invention is suitable for incorporating in the water base paint used for finish coating the car bodies. The aluminium pigment of the present invention can be incorporated in oil paints without showing any inconvenience.

The aluminium pigment of the present invention which is mainly coated with molybdic acid can be used with no environmental problem.

Examples

The following examples will more fully illustrate the present invention.

Examples 1 to 2

Aluminium flakes (Alpaste (trade name) 7670NS, $D_{50} = 15 \mu\text{m}$, produced by Toyo Aluminium K.K.) was weighed so that 200 g in terms of Al was present and placed in a beaker (3 litres), to which 1 l of propylene glycol monomethyl ether was added followed by stirring at 400 r.p.m., thereby a dispersion of aluminium flakes was prepared. The whole was cooled to 18°C. Independently, a predetermined amount of ammonium paramolybdate $(\text{NH}_4)_6\text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in 200 ml of demineralized water, thereby the treating solution was prepared.

To the dispersion of aluminium flakes, the treating solution was added dropwise and they were reacted for 1 hour at a predetermined pH at a liquid temperature of 15 to 20°C while stirring at 400 to 450 r.p.m. The amount of ammonium paramolybdate and pH on the treatment are shown in Table 1.

Then, a reaction product was decanted with the demineralized water three times so as to remove NH_4 ions and unreacted ammonium paramolybdate and filtered through a glass filter with suction. Then, the aluminium flakes on the filter were washed with propylene glycol monomethyl ether three times so as to completely remove the water and finally filtered with suction, thereby a first-treated aluminium pigment was obtained.

Examples 3 to 10 and Comparative Example 1 to 2

After redispersing the first-treated aluminium pigment (200 g in terms of Al) obtained in each of the above Examples in 108 g of propylene glycol monomethyl ether, a resultant dispersion was transferred into a kneader, to which a predetermined amount of a second treating agent previously dispersed in a small amount of propylene glycol monomethyl ether was added, and then mixed and kneaded for 30 minutes. The second treating agent used is shown in Table 1.

In Comparative Example 1, a commercially available aluminium pigment treated with chromic acid (STAPA HYDROLUX (trade name) 400, $D_{50} = 23 \mu\text{m}$, produced by Eckart-Werke AG) was used.

In Comparative Example 2, the aluminium flakes (Alpaste (trade name) 7670NS) used in Example 1 was used after replacing water with isopropyl alcohol.

In Comparative Example 3, the aluminium flakes treated in the same manner as Example 1, provided that 1 l of propylene glycol monomethyl ether was replaced with 1 l of propylene glycol monopropyl ether containing acetic acid (conc. 190 ppm) so that the reaction of aluminium with molybdate was conducted at pH 5.8, was used.

Table 1

| | first treatment | | second treatment | |
|-------------|--------------------------------|-----|-------------------------------|------------------|
| | ammonium p-molybdate (wt %) | pH | treating agent | amount (wt %) |
| Ex. 1 | 2.5 | 8.3 | - | - |
| Ex. 2 | 5.0 | 8.9 | - | - |
| Ex. 3 | 2.5 | 8.3 | Mo-Ca* | 5.0 |
| Ex. 4 | 5.0 | 8.9 | Mo-Ca* | 5.0 |
| Ex. 5 | 2.5 | 8.3 | Mo-Zn* | 5.0 |
| Ex. 6 | 5.0 | 8.9 | Mo-Zn* | 5.0 |
| Ex. 7 | 2.5 | 8.3 | LF MC400WR** | 5.0 |
| Ex. 8 | 2.5 | 8.3 | Mo-Ba* | 5.0 |
| Ex. 9 | 2.5 | 8.3 | Mo-Ba* | 5.0 |
| Ex. 10 | 2.5 | 8.3 | V ₂ O ₅ | 5.0 |
| Comp. Ex. 1 | - | - | - | - |
| Comp. Ex. 2 | - | - | - | - |
| Comp. Ex. 3 | 2.5 | 5.8 | - | - |

* Mo-Ca, Mo-Zn, Mo-Ba and Mo-Sr are calcium salt, zinc salt, barium salt and strontium salt of molybdic acid, respectively.

** trade name (Zn-Ca salt of molybdic acid, ex. Kikuchi Color and Chemicals Corporation)

Test

The stability of the aluminium pigment obtained in each of Examples 1 to 10 and Comparative Examples 1 to 3 in the water base metallic paint and the finish coating prepared from the same paint and the top clear paint were tested.

Formulation of water base metallic paint for base coating film:

| | | |
|----|---|---------|
| 5 | water soluble acrylic resin (Almatex (trade name) WA 911, produced by MITUSI TOATSU CHEMICALS INC.) | 28.16 g |
| | triethylamine | 1.14 g |
| | demineralized water | 44.8 g |
| 10 | melamine resin (Cymel 350, produced by MITSU CYANAMID) | 4.4 g |
| | isopropyl alcohol | 3.0 g |
| | transparent iron oxide (SICOTRANS (trade name) RED L1275D, produced by BASF) | 5.0 g |
| 15 | aluminium pigment (as Al) | 3.0 g |

Formulation of oily clear paint for top coating film:

| | | |
|----|---|---------|
| 20 | acrylic resin (Almatex (trade name) 110, produced by MITUSI TOATSU CHEMICALS INC.) | 140.0 g |
| | melamine resin (Uban (trade name) 20SE60, produced by MITUSI TOATSU CHEMICALS INC.) | 50.0 g |
| 25 | Solvesso 100 | 60.0 g |

Coating method:

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A steel plate previously electrodeposited with a primer was coated with the above paints in order using a SA-71 spray gun (IWATA TOSOKI KOGYO K.K.) and an automatic air coating device Model 310741 (SPRAY-MATION INC.) according to the 2C1B coating method, thereby a test piece was prepared. That is, the steel plate was coated with the water base metallic paint for base coating film so that the dried film had 13 μm in thickness and then previously dried in an air oven of 90°C for 10 minutes. Next, the oily clear paint for top coating film was coated so that the dried film had 40 μm in thickness followed by baking to cure in the air oven of 140°C for 30 minutes.

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Stability in the water base paint

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80 grams of the water base metallic paint was introduced in a flask, which was set on a water bath whose temperature was controlled to be 50°C. The cumulative volume of hydrogen gas produced for 7 days was determined. In Comparative Examples 2 and 3, the cumulative volume of hydrogen gas produced for 1 day was determined.

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The lower the cumulative volume of hydrogen gas is, the higher the stability of the pigment in the paint is.

Coating properties

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For testing the accelerated humidity resistance, the resultant finished film of the test piece was stored at the temperature of 50°C and the humidity of 98 % or more for 10 days. The changes in the color tone and the adhesion of the metallic film with the top clear film before and after the storage of the test piece were determined.

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The color tone (metallic luster IV value) of the metallic film was determined using a color measurement machine (ALCOPE (trade name) Model LMR-100, KANSAI PAINT CO., Ltd.). A desired metallic film stably shows the IV value higher than that in Comparative Example 2. The adhesion was determined in accordance with ASTM D3359 B (6 ranks). 3B or more is evaluated to be acceptable. The results are shown in Table 2.

Table 2

| | stability | coating properties | | | |
|-------------|-----------------|--------------------|----|-------------------|----|
| | gas volume (ml) | before IV adhesion | | after IV adhesion | |
| Ex. 1 | 3.0 | 202 | 5B | 205 | 4B |
| Ex. 2 | 2.0 | 195 | 5B | 196 | 4B |
| Ex. 3 | 0.5 | 197 | 5B | 198 | 5B |
| Ex. 4 | 0.0 | 185 | 5B | 185 | 5B |
| Ex. 5 | 0.5 | 195 | 5B | 195 | 5B |
| Ex. 6 | 0.0 | 187 | 5B | 186 | 5B |
| Ex. 7 | 0.5 | 198 | 5B | 199 | 5B |
| Ex. 8 | 0.5 | 198 | 5B | 198 | 4B |
| Ex. 9 | 0.5 | 190 | 5B | 192 | 4B |
| Ex. 10 | 0.5 | 195 | 5B | 195 | 4B |
| Comp. Ex. 1 | 1.0 | 193 | 4B | 195 | 3B |
| Comp. EX. 2 | >20 | 305 | 5B | 282 | 5B |
| Comp. Ex. 3 | >20 | 197 | 5B | 173 | 4B |

As shown in the above Table, the aluminium pigments of Examples 1 and 2 prepared by subjecting to only the first treatment showed very good color tone which was maintained after the test of accelerated humidity resistance. The aluminium pigments of Examples 3 to 10 prepared by subjecting the aluminium pigments of Examples 1 and 2 to the second treatment showed good color tone which was maintained after the test of accelerated humidity resistance. In addition, in the aluminium pigments of Examples 3 to 10, the volume of hydrogen gas produced is negligible. On the other hand, the aluminium pigment of Comparative Example 2 which was subjected to no treatment produced a large volume of hydrogen gas and as the result, its stability in the water base paint is very poor. The aluminium pigment of Comparative Example 1 which is the commercially available aluminium pigment treated with chromic acid produced a minor volume of hydrogen gas and showed good color tone, but the adhesion between the base coating film with the top coating film was slightly inferior. It had the tendency of showing the lowered adhesion after the test of accelerated humidity resistance. The lowering in adhesion is assumed to be due to the presence of a slight amount of residual chromic (VI) acid. The aluminium pigment of Comparative Example 3 which was obtained by reacting at an acidic condition produced a large volume of hydrogen gas, because it had an insufficient coatings of molybdic acid.

Quantitative determination of metal content (wt%)

The aluminium pigment was washed with acetone followed by powdering. After drying at 250°C for 15 minutes, the resultant powder was quantitatively determined by ICP analysis. The results are shown in Table 3.

Table 3

| | Al | Mo | Ca | Zn | Ba |
|------------|--------|-------|-------|-------|-------|
| Ex. 1 | 98.932 | 0.632 | 0.000 | 0.000 | 0.000 |
| Ex. 4 | 96.433 | 1.702 | 1.333 | 0.000 | 0.000 |
| Ex. 5 | 97.027 | 1.712 | 0.000 | 1.071 | 0.000 |
| Ex. 7 | 96.734 | 0.814 | 1.625 | 0.421 | 0.000 |
| Ex. 8 | 97.006 | 1.297 | 0.000 | 0.000 | 1.516 |
| Comp.Ex. 2 | 99.765 | 0.000 | 0.000 | 0.000 | 0.000 |
| Comp.Ex. 3 | 99.748 | 0.056 | 0.000 | 0.000 | 0.000 |

The content of Al was calculated by subtracting the total amount of metals other than Al such as Mo, Zn, Ca, Ba, V, Fe, Si, Cu and Ti from 100.

Claims

1. Aluminium flakes coated with molybdic acid in an amount of 0.1 to 10% by weight in terms of Mo based on Al.
2. Aluminium flakes according to claim 1 wherein at least one of a water-insoluble metal salt of molybdic acid and vanadium pentoxide is attached to the molybdic acid coating in an amount of 0.1 to 10% by weight in terms of metal based on Al.
3. An aluminium pigment comprising aluminium flakes as defined in claim 1 or 2 and a water-soluble solvent.
4. A pigment according to claim 3 which is in the form of a paste and wherein the water-soluble solvent is propylene glycol monomethyl ether.
5. A method for preparing aluminium flakes as defined in claim 1 comprising reacting aluminium flakes with ammonium molybdate in an alkaline aqueous solution.
6. A method according to claim 5 wherein the aluminium flakes to be reacted are dispersed in at least one water-soluble solvent selected from ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monopropyl ether and isopropyl alcohol.
7. A method according to claim 5 or 6 wherein the alkaline aqueous solution containing ammonium molybdate is added to the aluminium flakes or a dispersion thereof.
8. A method according to any one of claims 5 to 7 wherein the ammonium molybdate is ammonium paramolybdate.
9. A method according to any one of claims 5 to 8 wherein the reaction is conducted at a pH of 8 to 9.
10. A method according to claim 9 wherein the reaction is conducted at a pH of 8.3 to 9.8.
11. A method according to any one of claims 5 to 10 which further comprises mixing and kneading the coated aluminium flakes with at least one of a water-soluble metal salt of molybdic acid and vanadium pentoxide to form aluminium flakes as defined in claim 2.
12. A water base metallic paint or metallic coating film comprising aluminium flakes as defined in claim 1 or 2 or an aluminium pigment as defined in claim 3 or 4.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 6167

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|---|---|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.5) |
| P, X | DATABASE WPI Section Ch, Week 9252, Derwent Publications Ltd., London, GB; Class G01, AN 92-426415 & JP-A-4 318 181 (NIPPON PAINT CO.) 9 November 1992 * abstract * | 1, 5, 12 | C09C1/64 C09C3/06 C09D17/00 C09D7/12 |
| X | DATABASE WPI Section Ch, Week 8513, Derwent Publications Ltd., London, GB; Class G01, AN 85-077465 & JP-A-60 029 401 (PENTEL K. K.) 14 February 1985 * abstract * | 1 | |
| A | US-A-3 969 127 (D. R. ROBITAILLE ET AL.) | | |
| The present search report has been drawn up for all claims | | | TECHNICAL FIELDS SEARCHED (Int.Cl.5) C09C C09D |
| Place of search THE HAGUE | | Date of completion of the search 4 November 1993 | Examiner VAN BELLINGEN, I |
| CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | | | |

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